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Enhanced Deformation of Azobenzene-Modified Liquid Crystal Polymers under Dual Wavelength Exposure: A Photophysical Model

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Azobenzene-embedded liquid crystal polymers can undergo mechanical deformation in response to ultraviolet (UV) light. The natural rodlike *trans* state azobenzene absorbs UV light and isomerizes to a bentlike *cis* state, which disturbs the order of the polymer network, leading to an anisotropic deformation. The current consensus is that the magnitude of the photoinduced deformation is related to the statistical building up of molecules in the *cis* state. However, a recent experimental study [Liu and Broer, Nat. Commun. **6** 8334 (2015).] shows that a drastic (fourfold) increase of the photoinduced deformation can be generated by exposing the samples simultaneously to 365 nm (UV) and 455 nm (visible) light. To elucidate the physical mechanism that drives this increase, we develop a two-light attenuation model and an optomechanical constitutive relation that not only accounts for the statistical accumulation of *cis* azobenzenes, but also for the dynamic *trans-cis-trans* oscillatory isomerization process. Our experimentally calibrated model predicts that the optimal single-wavelength exposure is 395 nm light, a pronounced shift towards the visible spectrum. In addition, we identify a range of optimal combinations of two-wavelength lights that generate a favorable response for a given amount of injected energy. Our model provides mechanistic insight into the different (multi)wavelength exposures used in experiments and, at the same time, opens new avenues towards enhanced, multiwavelength optomechanical behavior.

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Introduction.—Responsive polymers now serve as new building blocks to create soft actuators. Light-activated systems are especially advantageous for remote control as their application does not require built-in electrodes and heating devices as in electrically or thermally actuated materials. The probably most-studied light responsive systems are liquid crystal (LC) polymers copolymerized with azobenzene [1–6]. Azobenzene functions as a photoisomerizable molecule that is covalently embedded in the LC polymeric skeleton and absorbs ultraviolet (UV) light leading to a transition from a rodlike *trans* state into a bentlike *cis* state. This process affects the orientational order of the neighboring LC network, producing an anisotropic optomechanical response, with a contraction along the director (i.e., the average orientation of the local molecules) and an expansion in the two perpendicular directions, accompanied by density changes. This actuation can be reversed by exposing the material to visible (VIS) light or heat, which accelerate the *cis* azobenzenes to fall back to the *trans* state. The current consensus in experimental [5,7–9] and theoretical studies [10–13] is that the amplitude of the photoinduced deformation is related to the statistical building up of molecules in the *cis* state. However, a recent experimental study [14] has revealed that this is only one side of the story. By exposing azobenzene-modified LC polymer (LC-Azo) samples to two light-emitting diode (LED) sources illuminating 365 nm UV light and 455 nm visible light, the largest response was found to occur under a combination of the two wavelengths, boosting the volume increase by a factor of 4 for intensities in the range of 100–300 $\mathrm{mW/cm^2}$.

To explain this phenomenon, we developed a two-wavelength light penetration model to predict the *trans*-to-*cis* and *cis*-to-*trans* conversions under mixed 365 and 455 nm exposure. A new constitutive relation is proposed that not only includes photoinduced deformations due to the statistical accumulation of *cis* isomers but also those due to the dynamic *trans-cis-trans* isomerization cycles. By combining this relation with the double-wavelength attenuation model, it will be demonstrated that our numerical simulations are able to reproduce and elucidate the experimental results and to predict optimal wavelengths under one- and two-light exposures.

Photophysics model.—A two-light nonlinear penetration model is developed based on previous theoretical studies [12,15]. In Ref. [15], a two-light model was proposed in which one light only activates the *trans*-to-*cis* forward reaction and the other only the *cis*-to-*trans* backreaction, thus accounting for two reactions during isomerization. Here, we extend our single-light illumination model [12] to double-wavelength exposure by accounting for the *trans*-to-*cis* forward reaction, the *cis*-to-*trans* backreaction, and the thermally activated backreaction for both lights, thus accounting for six reactions in total. We consider a LC-Azo coating with thickness w, subject to 365 and 455 nm light with intensities $I_{0,1}$ and $I_{0,2}$, respectively. We define a z axis pointing upwards, with the bottom at $z = 0$. The incident lights are propagating towards the negative z direction.

$I_1(z,t)$ and $\mathcal{I}_1(z,t) = I_1(z,t)/I_{0,1}$ denote the local and reduced light intensities inside the medium for the 365 nm light and $I_2(z,t)$ and $\mathcal{I}_2(z,t) = I_2(z,t)/I_{0,2}$ do the same for the 455 nm light. The conversion rates between the two isomers consist of five parts: the two photoinduced *trans*-to-*cis* forward reactions and the two photoinduced *cis*-to-*trans* backreactions by the two lights, and the thermal spontaneous backreaction with a characteristic time of τ. The conversion rate of the azobenzene isomers and the attenuation of the light intensities can be written as

$$\frac{\partial n_t}{\partial t} = -\eta_{t1}\Gamma_{t1}\zeta I_1(z,t)n_t(z,t) - \eta_{t2}\Gamma_{t2}\zeta I_2(z,t)n_t(z,t) + \eta_{c1}\Gamma_{c1}\zeta I_1(z,t)n_c(z,t) + \eta_{c2}\Gamma_{c2}\zeta I_2(z,t)n_c(z,t) + \frac{1}{\tau}n_c(z,t), \quad (1)$$

$$\frac{\partial I_1}{\partial z} = \gamma_1\Gamma_{t1}\zeta I_1(z,t)n_t(z,t) + \gamma_1\Gamma_{c1}\zeta I_1(z,t)n_c(z,t), \quad (2)$$

$$\frac{\partial I_2}{\partial z} = \gamma_2\Gamma_{t2}\zeta I_2(z,t)n_t(z,t) + \gamma_2\Gamma_{c2}\zeta I_2(z,t)n_c(z,t), \quad (3)$$

where n_t and $n_c = 1 - n_t$ are the volume fractions of the *trans* and *cis* azobenzenes, η_{ti} and η_{ci} ($i = 1, 2$) are the quantum efficiencies, and the Γ_{ti} and Γ_{ci} are the cross-section absorption coefficients (see also Ref. [12]). The parameter ζ is the polarization coefficient, which describes the probability of the isomers to absorb energy from the incoming light. It depends on the director alignment and the order parameter of the network, S. Here, we follow the experiments [14] and a diffuse light source is used so that $\zeta = [1 - SP_2(\cos\phi)]/3$, where ϕ is the angle between the director and the propagating direction of the light, and $P_2(x) = (3x^2 - 1)/2$ [12]. The constants $\gamma_i = \hbar\omega_i\rho_0\delta$ ($i = 1, 2$) depend on the Planck constant $\hbar$, the frequencies of the incident light ω_i, and the absolute number density of the chromophores $\rho_0\delta$ (ρ_0 is the total concentration of all mesogenic molecules before illumination and δ is the molar fraction of azobenzene dyes).

We use the dimensionless parameters α and β to quantify the magnitude of the source intensities relative to the internal material properties,

$$\alpha_1 = \eta_{t1}\Gamma_{t1}I_{0,1}\tau, \qquad \alpha_2 = \eta_{t2}\Gamma_{t2}I_{0,2}\tau,$$
$$\beta_1 = \eta_{c1}\Gamma_{c1}I_{0,1}\tau, \qquad \beta_2 = \eta_{c2}\Gamma_{c2}I_{0,2}\tau, \quad (4)$$

for the wavelength $\lambda_1 = 365$ nm (α_1, β_1) and $\lambda_2 = 455$ nm (α_2, β_2), and we define the attenuation lengths

$$d_{t1} = 1/\gamma_1\Gamma_{t1}, \qquad d_{c1} = 1/\gamma_1\Gamma_{c1},$$
$$d_{t2} = 1/\gamma_2\Gamma_{t2}, \qquad d_{c2} = 1/\gamma_2\Gamma_{c2} \quad (5)$$

for the *trans* (d_{t1}, d_{t2}) and the *cis* (d_{c1}, d_{c2}) azobenzenes. The attenuation lengths are related to α_i and β_i by

$$\frac{d_{t1}}{d_{c1}} = \frac{\beta_1}{\alpha_1}\eta_1, \qquad \frac{d_{t2}}{d_{c2}} = \frac{\beta_2}{\alpha_2}\eta_2, \quad (6)$$

where the two quantum efficiency ratios are defined as $\eta_1 = \eta_{t1}/\eta_{c1}$ and $\eta_2 = \eta_{t2}/\eta_{c2}$.

Now, by substituting Eqs. (4) and (5) into Eqs. (1)–(3) and dividing the light attenuation equations by the corresponding original intensities $I_{0,i}$, we obtain

$$\tau\frac{\partial n_t}{\partial t} = 1 + \beta_1\zeta\mathcal{I}_1(z,t) + \beta_2\zeta\mathcal{I}_2(z,t) - [1 + (\alpha_1 + \beta_1)\zeta\mathcal{I}_1(z,t) + (\alpha_2 + \beta_2)\zeta\mathcal{I}_2(z,t)]n_t(z,t), \quad (7)$$

$$\frac{\partial\mathcal{I}_1}{\partial z} = \left[\left(\frac{1}{d_{t1}} - \frac{1}{d_{c1}}\right)n_t(z,t) + \frac{1}{d_{c1}}\right]\zeta\mathcal{I}_1(z,t), \quad (8)$$

$$\frac{\partial\mathcal{I}_2}{\partial z} = \left[\left(\frac{1}{d_{t2}} - \frac{1}{d_{c2}}\right)n_t(z,t) + \frac{1}{d_{c2}}\right]\zeta\mathcal{I}_2(z,t). \quad (9)$$

We solve the problem in the photostationary state by setting the right-hand side of Eq. (7) equal to zero, which yields the stable volume fractions:

$$n_t(z) = \frac{1 + \beta_1\zeta\mathcal{I}_1(z) + \beta_2\zeta\mathcal{I}_2(z)}{1 + (\alpha_1 + \beta_1)\zeta\mathcal{I}_1(z) + (\alpha_2 + \beta_2)\zeta\mathcal{I}_2(z)}, \quad (10)$$

$$n_c(z) = \frac{\alpha_1\zeta\mathcal{I}_1(z) + \alpha_2\zeta\mathcal{I}_2(z)}{1 + (\alpha_1 + \beta_1)\zeta\mathcal{I}_1(z) + (\alpha_2 + \beta_2)\zeta\mathcal{I}_2(z)}. \quad (11)$$

By substituting Eq. (10) into Eqs. (8) and (9) we obtain two coupled nonlinear ordinary differential equations that can be solved for $\mathcal{I}_1(z)$ and $\mathcal{I}_2(z)$ through the thickness. The volume fractions $n_t(z)$ and $n_c(z)$ follow by substituting the intensities into Eqs. (10) and (11).

The solutions for $\mathcal{I}_1(z)$, $\mathcal{I}_2(z)$, $n_t(z)$, and $n_c(z)$ depend on eight system parameters, i.e., the dimensionless parameters α_i and β_i and the attenuation lengths for *trans* d_{ti} and for *cis* d_{ci}, $i = 1, 2$. To parametrize these values we use the experimental absorbance spectra of the *trans* and *cis* isomers [i.e., A_{t1}, A_{t2}, A_{c1}, and A_{c2} in Fig. 1(a)] in addition to the *cis* conversion measurements for mixed UV-VIS exposure at 100 mW/cm^2 UV intensity [see the red triangles in Fig. 1(b)]. In Fig. 1(b), only the data for 100 mW/cm^2 are used for parametrization; the results for 200 and 300 mW/cm^2 are predictions of the model. Details of the parametrization can be found in the Supplemental Material [16].

For pure UV exposure, the conversion from the *trans* to *cis* state is maximal compared to the other scenarios where 455 nm light is added [see Fig. 1(b)]. This is due to the fact that the additional 455 nm light accelerates the photoinduced backreaction so that at the photostationary state a lower *cis* volume fraction is reached. Inspection of the through-thickness two-light attenuation process [see Fig. S1(b) [16]] shows that the 455 nm light can penetrate much deeper than the 365 nm light, resulting in a pronounced backreaction to the *trans* state at larger depths, which is absent in the pure UV exposure [see Fig. S1(a) [16]].

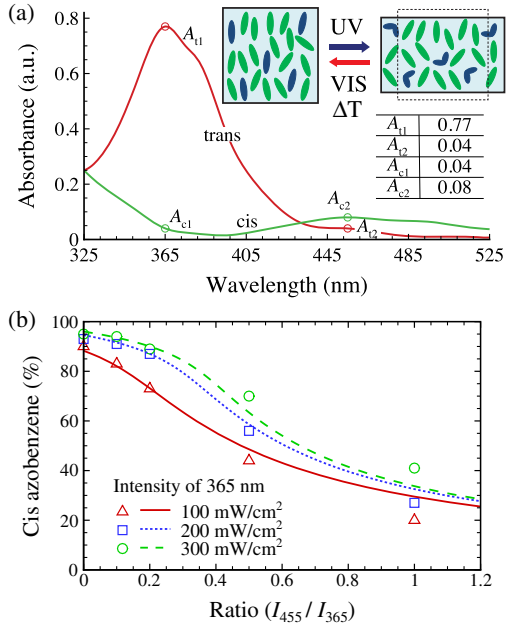

FIG. 1. (a) Measured absorbance spectra for the *trans* and *cis* azobenzenes [14]. The inset is a schematic representing the assumed mechanism for UV-responsive LC-Azo networks. (b) The numerical results (lines) and the experimental data [14] (symbols) for the averaged *cis* concentration as a function of the ratio between the exposure intensities of the 455 nm and the 365 nm wavelengths for three UV input intensities.

Photomechanical response.—In many previous theoretical studies, the photoinduced strain was commonly assumed to be linearly proportional to the *cis* volume fraction [8,11,12], or nonlinear but monotonically increasing [10,21]. However, the measured density decrease [14] (Fig. 2) shows that the largest response ensues when a small amount of 455 nm light is added, for which the corresponding *cis* state is not the highest [Fig. 1(b)]. Clearly, it is insufficient to only consider the increase in free volume due to the reduction in order by the statistical accumulation of the *cis* molecules. Also the cyclic *trans*-to-*cis* and *cis*-to-*trans* conversions contribute to free volume generation by order reduction. It has been demonstrated that the oscillatory conversions of the azobenzene molecules couple to the entire polymer network, bringing it out of its viscoelastic equilibrium [14]. Upon switching off the light, the polymer network mechanically relaxes in seconds, much faster than the *cis*-to-*trans* chemical relaxation, which is on the order of hours [14]. This difference in relaxation response corroborates the presence of two different contributions to free volume generation: that due to statistical *cis* accumulation and that due to dynamic *trans-cis-trans* oscillations.

Here, we propose a new constitutive relation in which we explicitly consider the dynamic *trans-cis-trans* conversions. The strain tensor components in the local coordinate system read

$$\varepsilon_{ij}^{\mathrm{ph}}(z) = P_{ij} n_c(z) + D_{ij} f(z), \tag{12}$$

where the first term on the right-hand side is the conventional static contribution (see, e.g., Ref. [12]) and the second term is a new dynamic term added to describe the effect of the continuous *trans-cis-trans* isomerization cycles. The subscripts in Eq. (12), i and j, refer to the local Cartesian reference system. The P_{ij} are the components of the photoresponsivity tensor [12], which macroscopically link the *cis* accumulation to a decrease in order leading to an increase in free volume. The D_{ij} have a similar interpretation as the P_{ij} but account for the order reduction and free volume generation due to the dynamics of the isomers. The function f is phenomenological, resembling a continuous probability density function [22]:

$$f = n_\tau(z)\left[A + B\left(\frac{\sum \alpha_k \mathcal{I}_k}{\sum(\alpha_k \mathcal{I}_k + \beta_k \mathcal{I}_k)} - C\right)^2\right]^{-3}, \tag{13}$$

where A, B, and C are constants and the subscript k ($k = 1, 2$) refers to the two lights. The function f describes the cooperative effect between the oscillating azobenzenes and the distortion of the viscoelastic polymer network to which

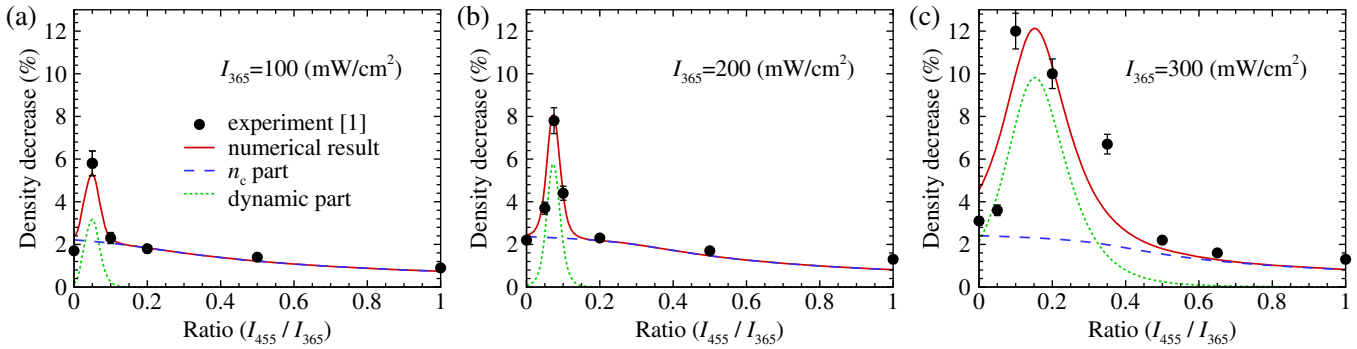

FIG. 2. The numerical (solid lines) and experimentally measured [14] (circles) density decrease for various input UV intensities: I_{365} = (a) 100, (b) 200, and (c) 300 mW/cm^2. The solid red curves show the total density changes (numerical results) and the other two colors show the two contributions, i.e., the effect due to the *cis* isomer accumulation (dashed blue) and the dynamic *trans-cis-trans* oscillation cycles (dotted green).

they are crosslinked and how this depends on the combination of UV and VIS illumination. The driving force for the dynamic contribution is

$$n_\tau = 1 + \beta_1 \zeta \mathcal{I}_1(z) + \beta_2 \zeta \mathcal{I}_2(z), \tag{14}$$

the volume fraction of azobenzenes undergoing backward *cis*-to-*trans* transitions during the time τ [see Eq. (7)]. Since the forward rate equals the backward rate in the photostationary state, n_τ also represents the volume fraction of *trans*-to-*cis* transitions during time τ, so that a large n_τ corresponds to a large dynamic cycling rate.

The density decrease (equal to the free volume increase) of a sample can be obtained by calculating the averaged volumetric strain through the thickness $\int_0^w \varepsilon_{\mathrm{vol}}^{\mathrm{ph}}(z)dz/w$, where $\varepsilon_{\mathrm{vol}}^{\mathrm{ph}}(z)$ is equal to the trace of the strain tensor given in Eq. (12).

We conduct a parametrization process to obtain the values of all unknown constants (see the Supplemental Material [16]), i.e., the material responsivity parameters P_{ii} and D_{ii} (with $i = 1, 2, 3$), as well as A, B, and C in the function f, based on measured density decreases [14] and the light parameters used in Fig. 1(b) (listed in Table S1 [16]). The numerical results are shown in Fig. 2, with all the obtained parameters are listed in Table S2 [16].

From Fig. 2 we observe that the dynamic effect only occurs under specific intensity combinations. Outside those ranges, such as the pure 365 nm illumination or a mixed exposure with comparatively large 455 nm intensity (ratios larger than 0.5), the dynamic effects are small and almost all the deformations are attributed solely to the *cis* accumulation. One possible explanation for this limitation is that it needs a special energy input that can simultaneously boost *trans*-to-*cis* and *cis*-to-*trans* transitions to an appropriate level to sustain the generated free volume, which cannot be realized by purely exposing either 365 or 455 nm light. The dynamic contribution increases with light intensity. For the 100 mW/cm^2 365 nm light illumination, the static n_c contribution is comparable to the dynamic contribution, but for the 300 mW/cm^2 intensity, even with an increase of the *cis* concentration [Fig. 1(b)], the n_c contribution is much lower than the dynamic counterpart. It should be noted that the function f describes the interplay between the oscillating azobenzenes and the distortion of the viscoelastic polymer network in a phenomenological sense. The precise molecular origin of this oscillatory, cooperative effect remains a subject for further investigation.

Optimal wavelength.—The discrepancy between the *cis* conversion level and the optomechanical response under double-wavelength illumination brings in a new question: If a single-light exposure is used, which wavelength is optimal?

To answer this question, one needs the light parameters for an arbitrary wavelength λ_i (365 nm $\leq \lambda_i \leq$ 455 nm), i.e., the dimensionless parameters α_i and β_i, the attenuation length for *trans* d_{ti}, and the quantum efficiency ratio $\eta_i = \eta_{ti}/\eta_{ci}$. Here, we follow the same procedure as in the parametrization for the two-wavelength illumination, but now applied for one wavelength only. To obtain all the necessary input parameters for λ_i, we assume the quantum efficiencies η_{ti} and η_{ci} follow an *S*-shaped variation between the quantum efficiencies of the 365 and 455 nm wavelengths and make use of the absorbance spectra A_{ti} and A_{ci} from Fig. 1(a) (see the section entitled "Optimal wavelength" in the Supplemental Material [16]). The prediction for the density decrease under single LED exposure is given in Fig. 3 for three different input intensities. Interestingly, the optimal wavelength undergoes a pronounced shift of 30 nm towards the visible regime. The optimal wavelength does not only generate a high *cis* conversion level, it also triggers a considerable dynamic effect with the help of the enhanced *cis* absorbance. This result corroborates recent experiments in which not an UV but a higher wavelength light source was selected to trigger azobenzene-embedded systems, such as blue-green light [23,24] and other illumination scenarios [4,25–27].

Next we ask the following question. What is the optimal combination of wavelengths for a two-light illumination system? The optimization parameters are the two wavelengths λ_1 and λ_2, and their intensities. We assume that the total input energy is 300 mW/cm^2, thus addressing the question of which system features an optimal efficiency. The result is shown in Fig. 4 by a three-dimensional contour plot for the density decrease as a function of the two wavelengths and their intensities. Clearly, for every energy distribution, there always exists a wavelength with a comparatively large response in which the dynamic effect can be exploited: choosing near-UV light, emitting at the largest intensity, and letting the other wavelength be close to the effective *cis* absorbance range, which leads to a relatively high *cis* conversion and simultaneously a large, effective *trans-cis-trans* cycling rate. This result quantitatively matches the light-induced motion of azobenzene crystal plates [28], in which a mixed 200 mW/cm^2 365 nm and 60 mW/cm^2 465 nm exposure yields the most favorable deformation.

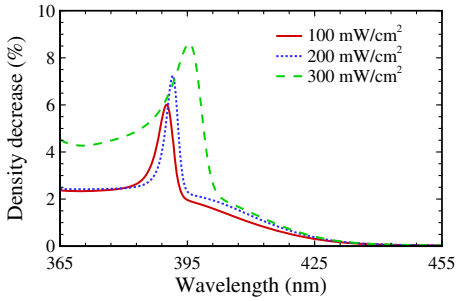

FIG. 3. Predicted density decrease as a function of wavelength for single-light illumination.

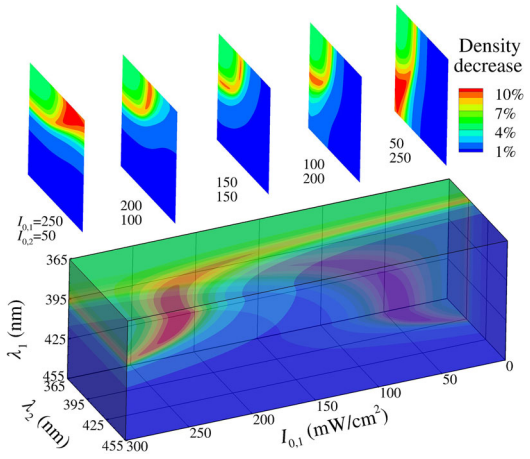

FIG. 4. Design box for maximizing the optomechanical response under two-light illumination with arbitrary wavelengths. The sum of the power is 300 mW/cm^2 and the intensities are $I_{0,1}$ and $I_{0,2} = 300 - I_{0,1}$ for wavelengths λ_1 and λ_2, respectively.

The above single- and double-wavelength approaches can be extended to multiple sources, such as LC actuators containing azo derivatives exposed to light sources emitting multiple wavelength peaks, like mercury light [29,30] and actinic light [9,31,32]. This would allow us to filter out wavelengths that have a minimal contribution, leading to a higher system efficiency.

It should be noted that our analysis assumes isothermal conditions, so that the predictions are valid for exposure scenarios in which temperature changes are limited. For systems undergoing a considerable temperature increase under strong intensities [30,33], one needs to take the self-heating into account since the characteristic fall-back time of the *cis* azobenzene, τ, decreases with temperature, leading to reduced light parameters α and β [see Eq. (4)], and thus affects the light attenuation and the constants in Eq. (13).

Conclusion.—In short, we have developed a double-wavelength attenuation model that accurately describes the *trans* and *cis* distributions in films of azobenzene-embedded LC polymers. In addition, we have formulated an experimentally calibrated photomechanical constitutive relation that is able to differentiate between strains resulting from the statistical *cis* accumulation and the dynamic *trans-cis-trans* isomerization cycles. Our results show that the optimal single wavelength light for the studied system is not UV light, but 395 nm light, a considerable shift towards the visible spectrum. Our model provides fundamental mechanistic insight into the different wavelength exposures used in experiments [4,14,23] and opens the possibility to explore the maximal optomechanical response under various multiwavelength illumination configurations.

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[1] T. H. Ware, M. E. McConney, J. J. Wie, V. P. Tondiglia, and T. J. White, Science **347**, 982 (2015).
[2] H. Finkelmann, E. Nishikawa, G. G. Pereira, and M. Warner, Phys. Rev. Lett. **87**, 015501 (2001).
[3] C. L. van Oosten, C. W. Bastiaansen, and D. J. Broer, Nat. Mater. **8**, 677 (2009).
[4] J. Lv, Y. Liu, J. Wei, E. Chen, L. Qin, and Y. Yu, Nature (London) **537**, 179 (2016).
[5] S. Iamsaard, E. Villemin, F. Lancia, and S.-J. Aßhoff, S. P. Fletcher, and N. Katsonis, Nat. Protoc. **11**, 1788 (2016).
[6] T. J. White and D. J. Broer, Nat. Mater. **14**, 1087 (2015).
[7] D. Liu and D. J. Broer, Angew. Chem., Int. Ed. Engl. **126**, 4630 (2014).
[8] C. L. van Oosten, D. Corbett, D. Davies, M. Warner, C. W. Bastiaansen, and D. J. Broer, Macromolecules **41**, 8592 (2008).
[9] M. Yamada, M. Kondo, R. Miyasato, Y. Naka, J.-i. Mamiya, M. Kinoshita, A. Shishido, Y. Yu, C. J. Barrett, and T. Ikeda, J. Mater. Chem. **19**, 60 (2009).
[10] M. Knežević, M. Warner, M. Čopič, and A. Sánchez-Ferrer, Phys. Rev. E **87**, 062503 (2013).
[11] D. Corbett and M. Warner, Phys. Rev. Lett. **99**, 174302 (2007).
[12] D. Liu, L. Liu, P. R. Onck, and D. J. Broer, Proc. Natl. Acad. Sci. U.S.A. **112**, 3880 (2015).
[13] J. Choi, H. Chung, J.-H. Yun, and M. Cho, Appl. Phys. Lett. **105**, 221906 (2014).
[14] D. Liu and D. J. Broer, Nat. Commun. **6** 8334 (2015).
[15] M. Warner and R. J. Blaikie, Phys. Rev. A **80**, 033833 (2009).
[16] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.119.057801 for the detailed parametrization of the light parameters and the optomechanical relation, which includes Refs. [17–20].
[17] A. D. McNaught and A. D. McNaught, *Compendium of Chemical Terminology*, Vol. 1669 (Blackwell Science, Oxford, 1997).
[18] Y. Zhao and T. Ikeda, *Smart Light-Responsive Materials: Azobenzene-Containing Polymers and Liquid Crystals* (John Wiley & Sons, New York, 2009).
[19] D. J. Broer, G. P. Crawford, and S. Zumer, *Cross-Linked Liquid Crystalline Systems: From Rigid Polymer Networks to Elastomers* (CRC Press, Boca Raton, 2011).
[20] C.-C. Li, C.-W. Chen, C.-K. Yu, H.-C. Jau, J.-A. Lv, X. Qing, C.-F. Lin, C.-Y. Cheng, C.-Y. Wang, J. Wei *et al.*, Adv. Opt. Mater. **5**, 1600824 (2017).
[21] Y. Lin, L. Jin, and Y. Huo, Int. J. Solids Struct. **49**, 2668 (2012).
[22] J. K. Ord, *Families of Frequency Distributions* (Hafner Publishing Co., London, 1972), Vol. 30.
[23] T. J. White, N. V. Tabiryan, S. V. Serak, U. A. Hrozhyk, V. P. Tondiglia, H. Koerner, R. A. Vaia, and T. J. Bunning, Soft Matter **4**, 1796 (2008).
[24] J. Ma, Y. Li, T. White, A. Urbas, and Q. Li, Chem. Commun. (Cambridge) **46**, 3463 (2010).
[25] C. Zong, Y. Zhao, H. Ji, X. Han, J. Xie, J. Wang, Y. Cao, S. Jiang, and C. Lu, Angew. Chem., Int. Ed. Engl. **55**, 3931 (2016).

[26] H. Ji, Y. Zhao, C. Zong, J. Xie, X. Han, J. Wang, J. Zhao, S. Jiang, Y. Cao, and C. Lu, ACS Appl. Mater. Interfaces **8**, 19127 (2016).
[27] Y. Li, O. Rios, J. K. Keum, J. Chen, and M. R. Kessler, ACS Appl. Mater. Interfaces **8**, 15750 (2016).
[28] E. Uchida, R. Azumi, and Y. Norikane, Nat. Commun. **6**, 7310 (2015).
[29] D. Liu, C. W. M. Bastiaansen, J. M. J. den Toonder, and D. J. Broer, Angew. Chem., Int. Ed. Engl. **51**, 892 (2012).
[30] J. J. Wie, M. R. Shankar, and T. J. White, Nat. Commun. **7**, 13260 (2016).
[31] T. Ikeda, M. Nakano, Y. Yu, O. Tsutsumi, and A. Kanazawa, Adv. Mater. **15**, 201 (2003).
[32] J. J. Wie, S. Chatterjee, D. H. Wang, L.-S. Tan, M. R. Shankar, and T. J. White, Polymer **55**, 5915 (2014).
[33] K. Kumar, A. P. Schenning, D. J. Broer, and D. Liu, Soft Matter **12**, 3196 (2016).